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Submitted to the Journal of Chemical Physics

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FROM MASS SPECTROMETRY

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October 1980

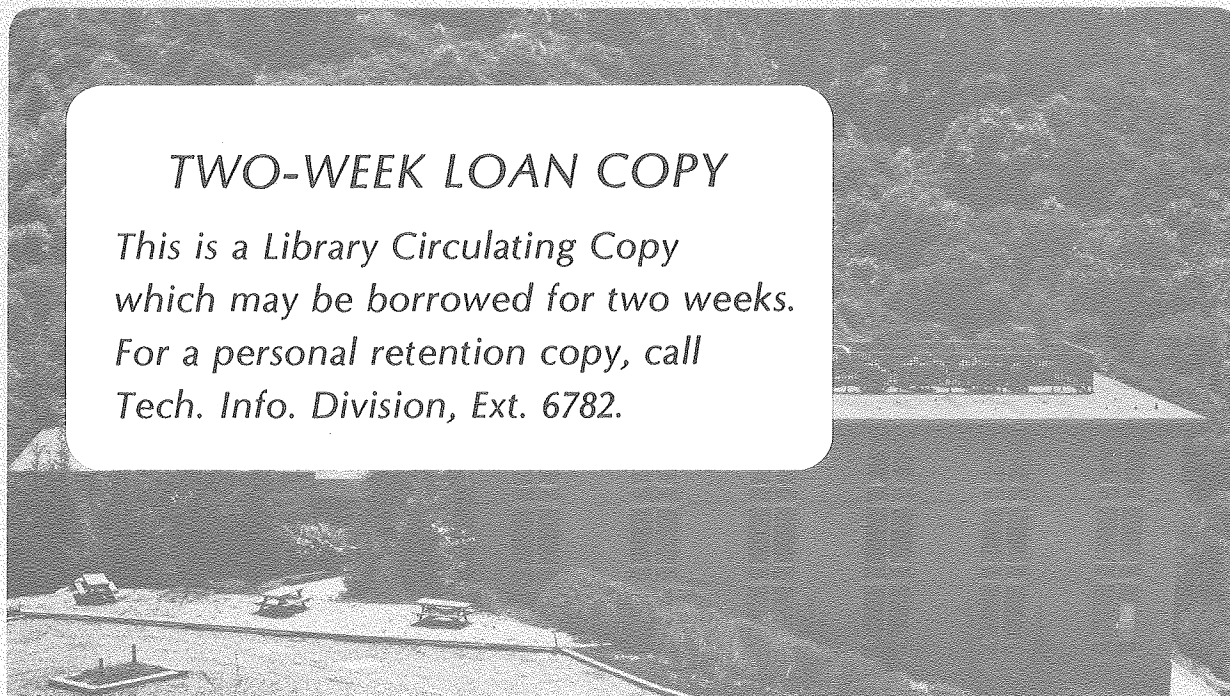
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LBL-11763 v. 2

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Dissociation Energies of Molecules with Very Heavy
Atoms from Mass Spectrometry

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In a series of excellent mass-spectrometric investigations Gingerich and associates have measured the dissociation energies of many molecules including heavy atoms. In the "third law" method of treating the data, the partition functions are required. Thus the electronic partition function of the molecule is needed. For molecules with very heavy atoms, relativistic effects yield large spin-orbit splittings and in some cases this reduces the electronic partition function by a significant factor. This is illustrated below for the two cases Pb_2^1 and BiLi^2 .

In each of these cases lighter analogs Si_2 and SbH have $^3\Sigma^-$ ground states; hence the assumption made^{1,2} of an electronic multiplicity of 3 was reasonable, *prima facie*. But for BiH it is known³ that the $J=1$ component of $^3\Sigma^-$ is 4917 cm^{-1} higher in energy than the $J=0$ component. Thus, the case c or relativistic notation 1 and 0^+ is more appropriate and there is a single 0^+ ground state. Even at the temperature of experiment, 1100 K, the population of the doubly degenerate 1 state is less than 1%. This spin-orbit splitting is essentially a property of the bismuth atom, and it should not be much different in BiLi . Thus the electronic partition function should be reduced from 3 to 1 and the function $-(G_T - H_0^\circ)/T$ reduced by $R \ln 3$. The effect of this change is shown in Table I which includes both the original and revised values of ΔH_0° of dissociation from the third law. In addition the temperature dependence of the equilibrium constant yields a less precise value of

ΔH at the temperature of the experiment and this can be converted to zero Kelvin. This is called the second law result and is not affected by this change in molecular parameters. While the 2nd law value for BiLi still differs from the more precise 3rd law value by more than the apparent uncertainty, the deviation is reduced by 10 kJ mol^{-1} by the use of the correct electronic multiplicity.

In the case of Pb_2 there are recent spectroscopic data from Bondybey and English⁴ which confirms the ground state as 0_g^+ , a single state. While there is no explicit value for the energy of excitation to the 1_g state (the other component of $3\Sigma_g^-$), it is expected to be comparable to the spin-orbit splitting ($3P_1 - 3P_0$) in the atomic spectrum, 7819 cm^{-1} . Thus it is expected that the 1_g population at 1000 K will be negligible. For Pb_2 there is also a small revision⁴ in the vibration frequency, 110 instead of 119 cm^{-1} . These two changes yield the results shown in Table I. The third law result for Pb_2 now agrees very well with the second law value and gives much greater assurance of the correctness of the new selected value of $83 \pm 1 \text{ kJ/mole}$ ($0.86 \pm 0.01 \text{ eV}$).

Since the vibration frequency and bond distance in BiLi were both estimated, there is further uncertainty in the third law result.

I have no reason to change these estimates, but the additional uncertainty is recognized by the (?) in Table I.

Similarly large spin-orbit splittings may be expected for other molecules with very heavy atoms; thus one should be cautious in adopting the electronic partition function of a lighter analog.

This research was supported by the Division of Chemical Sciences, Office of Basic Energy Science, U. S. Department of Energy under Contract No. W-7405-ENG-48.

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Table I. Revision of the Dissociation Energies of Pb_2 and BiLi

	Pb_2	BiLi
Approximate temperature	1000	1100 K
Original ΔH_0° of diss. (3rd law)	74 ± 1	$135.7 \pm 1.1 \text{ kJ mol}^{-1}$
Revised ΔH_0° of dissoc. (3rd law)	82.5 ± 1	$145.7 \pm ? \text{ kJ mol}^{-1}$
ΔH_0° of diss. (2nd law) unchanged	84 ± 2	$160 \pm 7 \text{ kJ mol}^{-1}$
Selected value	83 ± 1	$150 \pm 5 \text{ kJ mol}^{-1}$
Selected value in eV	$0.86 \pm .01$	$1.55 \pm .05 \text{ eV}$